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Sampling Hop Yards and Chemical Determination of Hop Maturity

July 1960

Agricultural Research Service
U. S. DEPARTMENT OF AGRICULTURE

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Appreciation is expressed to Mr. R. G. Wright of P. Ballantine and Sons, whose assistance and encouragement was responsible for the initiation of the cooperative project in 1956.*

*Mention of this firm does not constitute endorsement of its products by the U. S. Department of Agriculture over similar firms or products not mentioned.

SAMPLING HOP YARDS AND CHEMICAL DETERMINATION OF HOP MATURITY[1/]

S. T. Likens[2/]

INTRODUCTION

With the advent of increased information regarding the contribution of alpha-acid and essential oils of hops to the brewing process, the brewing industry is imposing new demands upon the quality of hops. A major factor in hop quality is the degree of maturity. Under-ripeness causes the product to be short of its potential in α-acid and oil content. Over-ripeness causes brittle hops which tend to shatter easily, have a high broken cone content with an accompanying loss in lupulin, and which exhibit poorer storage characteristics.

To meet the demands of the trade it is often desirable to sample a yard at intervals throughout the growing season to follow the progress of its quality status and to use this information as a guide in determining the most favorable time to harvest.

The purpose of this report is to give in some detail the method which is being developed by Agricultural Research Service, U. S. Department of Agriculture, at its Corvallis, Oreg. Station for monitoring the maturity of hop fields.

GENERAL APPROACH

Samples must be collected from a field at intervals throughout the season. The frequency should increase from every week or 10 days early in the season to every 2 or 3 days near harvest. The determination of the α-acid content is of more general interest, but in some cases it is desirable to determine the oil content. These two items satisfy the requirements imposed by the consumer. In addition a grower may be interested in the progress of the yield of the yard. This may be determined by maintaining a record of the average weight of the cones. In order that all samples are strictly comparable it is necessary that the moisture content of each sample be determined and that final results recorded on a dry-weight (moisture-free) basis.

1/ Cooperative investigations between the Crops Research Division, Agricultural Research Service, U. S. Department of Agriculture, and the Oregon Agricultural Experiment Station.

2/ Chemist, Crops Research Division, Agricultural Research Service, U. S. Department of Agriculture, at Oregon State College, Corvallis, Oreg.

As samples are taken and analyzed, the data are plotted on graph paper and picking is initiated when the curves indicate maturity. Obviously four curves might be developing simultaneously for a single field--α-acid, oil, cone weight, and dry matter. The consideration given each curve in the harvesting decision depends upon the use to which the crop is to be put. This will be discussed under INTERPRETATION OF RESULTS.

FIELD SAMPLING

Every effort must be made to keep sample variation small yet maintain an adequate sampling of the field. Since all hops in the field will be harvested, it is essential that a representative sample of cones be obtained regardless of size, shape, degree of maturity, and other factors. The wide variations found within a field, necessitate the obtaining of fairly large samples. Because of this, it has been our practice to sample as randomly as possible from about 600 plants. No fixed sampling plan can be followed because of variation in the size and shape of the fields. In general, however, it has been satisfactory to divide a field into three areas and collect about 1-1/2 lbs. from each. If the field is small, two 4- to 6-row sections from each of the three areas will be adequate, the actual sampling can be done by taking a few hops from each hill in a zigzag course, down one section and back the other. If the field is large, it is preferable to sample two adjacent sections at a time, as illustrated in figure 1. After the areas are sampled the hops are composited and mixed well. Twelve-quart pails are suitable for picking, and large polyethylene freezer bags serve well for compositing and transporting the sample. These should be kept as cool as possible until they arrive at the laboratory. To sample the same areas on successive dates, it is well to draw a sketch of the field indicating the sections to be sampled.

The amount of hops collected by the method described above is sufficient for the determination of oil content, α-acid, cone weight, moisture content and leaves about 2 lbs. which can be dried to about 1/2 lb. for a permanent sample, if that is desirable. If fewer determinations are required, the sample size can be reduced, although the area from which it comes should remain the same in order to get adequate representation of the field.

Because of the practical limitations of sampling at heights beyond reach, the assumption must be made that while those hops within reach may not be as rich, they nevertheless give a reasonable indication of the maturity of the whole crop.

At harvest all hills, all vines, and all hops along a side arm should be taken without consideration as to their size, color, or degree of maturity. Therefore, in sampling, personal bias must be removed as completely as possible. The best way to do this is for the sampler, before he has an opportunity to come to a decision regarding his own feelings concerning their beauty or position, should walk rapidly while picking a sample and selecting a few hops from each vine.

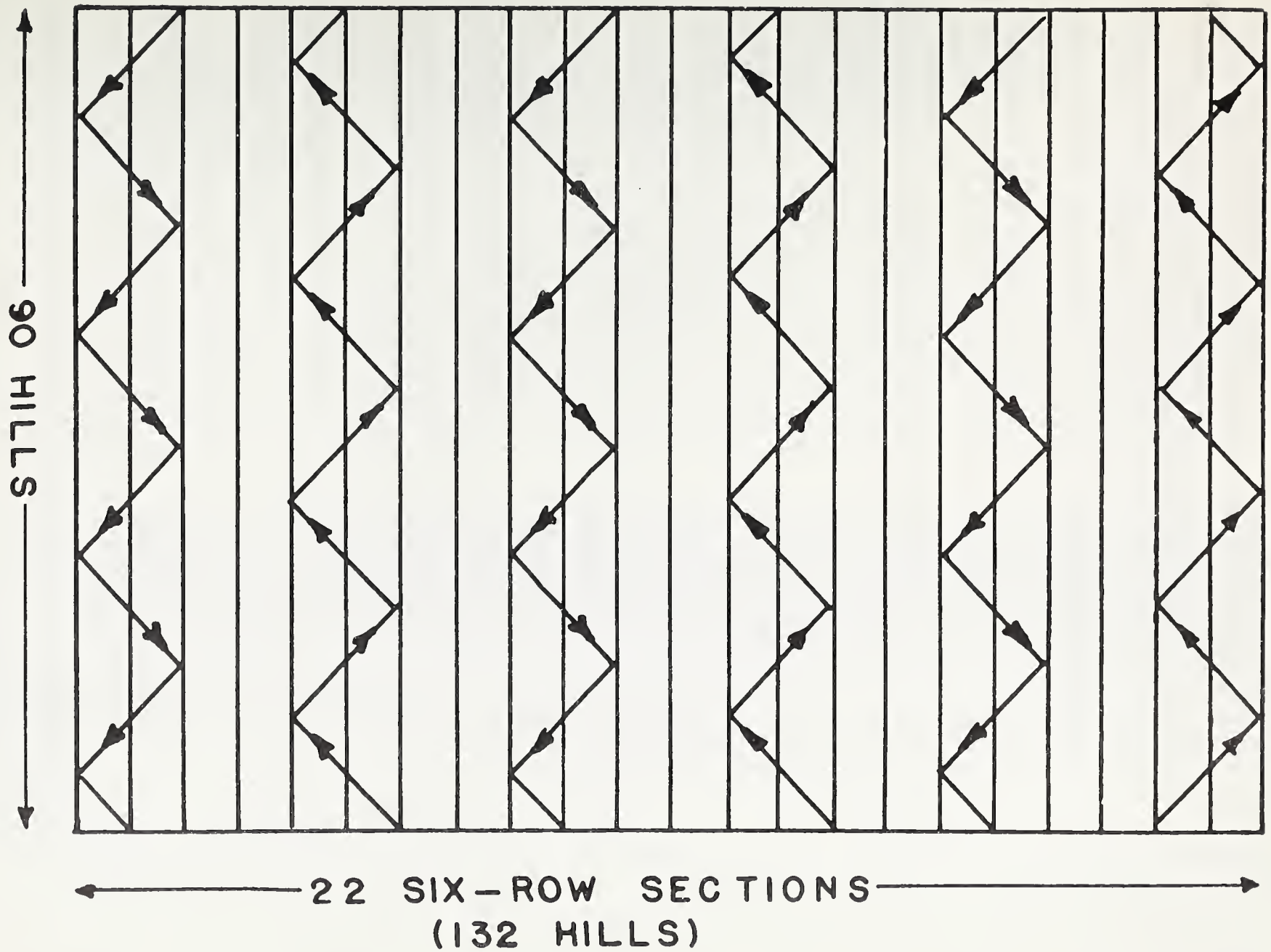

Figure 1.-- A typical sampling plan for a 15-acre field with 6-row sections. Lines and arrows indicate route and direction of sampling. In this example 540 hills would be sampled in 3 round trips through the field.

LABORATORY HANDLING

Samples should be taken to the laboratory as soon as possible, preferably within 1 or 2 hours. If longer delays are necessary, steps should be taken to refrigerate the samples until they can be analyzed.

Determination of Moisture Content (Toluene Distillation Method)

Weigh 110.0 g. of green hops in a suitable container (pint freezer cartons work well), and transfer to a 1 liter flask.3/ Add 300 ml. of toluene and attach the flask to a 100-ml. moisture trap and reflux condenser as shown in figure 2. Boil until all moisture is removed, usually 2 hours is sufficient. Make sure that no droplets of water are left hanging on the walls of the trap and that the water layer is free of toluene.

3/ This should be done quickly so that a minimum amount of moisture is lost between weighing and closing the flask. If cone weight is needed, the cones are counted as they are transferred.

Figure 2.-- Apparatus for the determination of moisture by toluene distillation showing the special type distillation receiver required for 110 g. of green hops.

It is imperative that the moisture trap be allowed to cool to room temperature before readings are taken. Read the milliliters of water collected and calculate as follows:

$$\text{Dry matter (g)} = \text{sample weight} - \text{milliliters of water} \quad (1)$$

$$\text{Percent dry matter} = \frac{\text{grams dry matter} \times 100}{\text{sample weight}} \quad (2)$$

An example of a moisture content determination can be found in the Appendix.

Determination of Cone Weight

To find the average cone weight it is necessary only to count the number of cones which make up the moisture sample. The calculation is:

$$\text{Average cone weight (mg.)} = \frac{\text{green weight} \times \text{percent dry matter}}{\text{number of cones counted}} \times 10 \quad (3)$$

An example of cone weight determination can be found in the Appendix.

Determination of Alpha-acid in Green Hops

The method used in this laboratory is a slight modification of the conductometric method of Hartong and Isebaert.[4/] The apparatus is shown in figure 3 and examples of data and calculations are shown in the Appendix. In a Waring Blendor[5/], 30 g. of green hops are extracted for 5 minutes with 100 ml. of chloroform. The extract is filtered through cotton as quickly as possible in order to minimize evaporation, collected in a narrow necked flask and stoppered. A 15 ml. aliquot is diluted with sufficient methanol to cover the electrodes of the dip cell. The solution is stirred with an automatic stirrer until a steady reading is obtained on the conductivity bridge. Titration is carried out with 0.25 ml. to 0.50 ml. increments, (at least 5 points prior to the end point should be obtained), of fresh 2 percent lead acetate [$Pb(C_2H_3O_2)_2.3H_2O$; M.W. = 379.35] in methanol (see data sheet in Appendix). If the hops are richer than average, that is, over 6 percent α-acid, 4 percent lead acetate might be desirable. After each increment the solution is allowed to equilibrate and a reading is made.

4/ Hartong, B. D. and Isebaert, I., The Conductometric Determination of α-acids in Green Hops on the Farm. Wall. Lab. Communs. 22: 17-23 (1959)

5/ Mention of specific product in this paper is not to be construed as a recommendation or endorsement of them by the Department of Agriculture over similar products not mentioned.

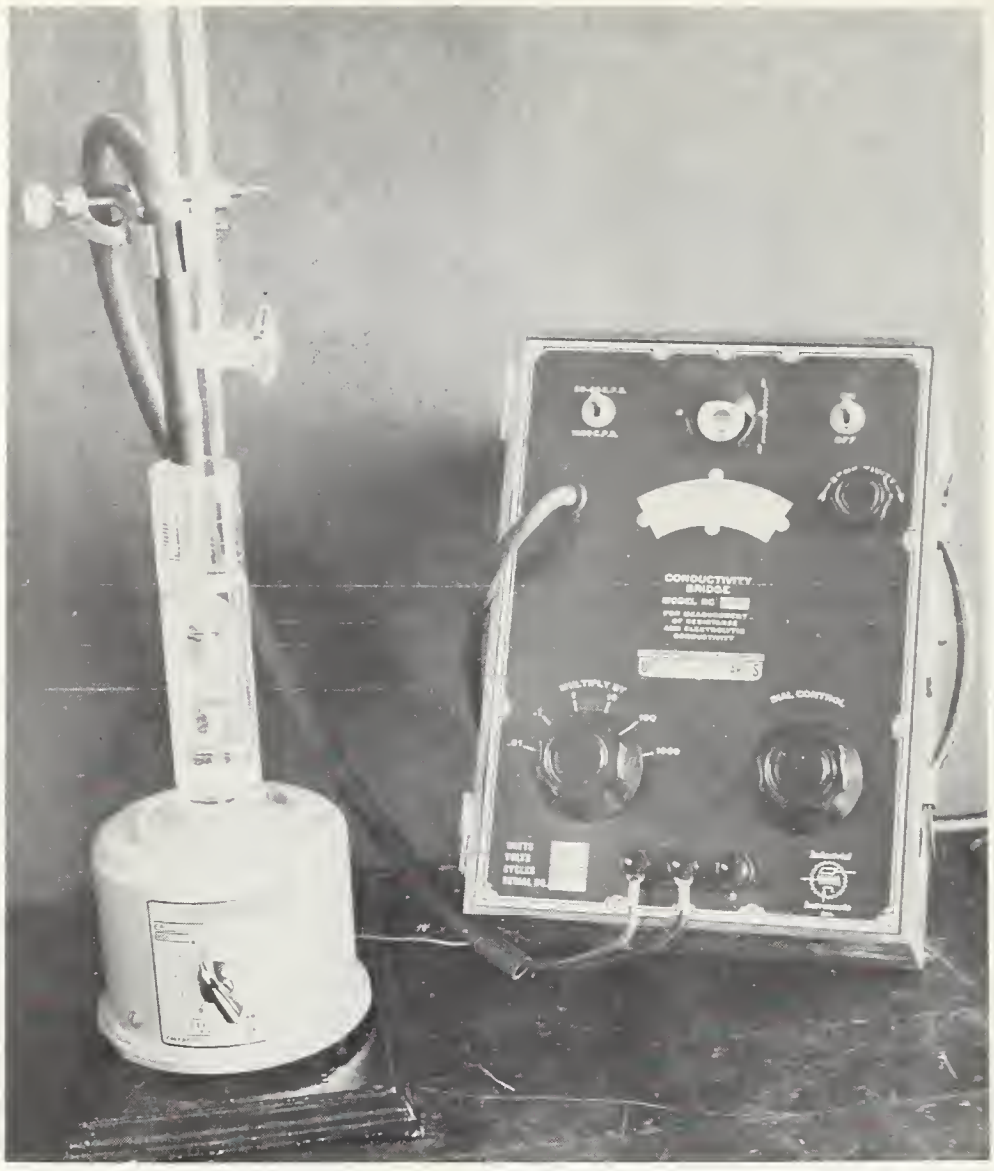

Figure 3.-- Assembly used for the conductometric titration of α-acid.

Little change in conductivity is noticed until all α-acid is precipitated, after which there is a sharp rise. Four or five readings should be taken beyond the end point. If the readings are in ohms resistance, it is necessary to calculate mhos conductivity (1/ohms) for each reading. The mhos conductivity is then plotted against milliliters of lead acetate and lines drawn through each arm of the graph (see figure 10, Appendix).

The intersection of these lines is the end-point of the titration, and the calculation is:

$$\text{Percent } \alpha\text{-acid (dry basis)} = \frac{\text{ml. lead acetate} \times \text{pct. lead acetate}}{\text{percent dry matter}} \times 20.97 \quad (4)$$ [6/]

where "ml. lead acetate" is the end-point of the titration, "percent lead acetate" is the strength of the titrant, "percent dry matter" is found from the moisture determination previously described and 20.97 is the factor necessary to account for constants in the formula. Between titrations the dip cell should be cleaned with a 50 percent solution of acetic acid in toluene and rinsed thoroughly with methanol. Drift in readings prior to the end-point can usually be traced either to a poorly rinsed dip cell or to a change in temperature during the titration. To standardize the titrant it is necessary only to substitute 4.0 ml. of 0.10 N H_2SO_4 for the sample and titrate as usual. Construction of the graph (see figure 9 in Appendix) is the same and the milliliters of lead acetate found at the end-point is applied to the following equation:

$$\text{Percent lead acetate} = \frac{7.58}{\text{ml. lead acetate}} \quad (5)$$ [7/]

Because the strength of this reagent seems to change significantly from day to day, it is necessary to standardize it frequently.

Determination of the Oil Content of Green Hops

Analysis for the oil content is carried out as described by Wright

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6/ The complete equation is:

$$\text{Percent } \alpha\text{-acid (D.B.)} = \frac{\text{ml. } PbAc_2.3H_2O \times \text{pct. } PbAc_2.3H_2O \times \text{eq.wt. } \alpha\text{-acid} \times \text{extract vol.} \times 100}{\text{eq.wt. } PbAc_2 3H_2O \times \text{aliquot} \times \text{sample wt.} \times \text{pct. dry matter}}$$

The constant in equation (4) is based on 358 which is the average M.W. for α-acid containing 30 percent cohumulone.

7/ The complete equation is:

$$\text{Percent } PbAc_2.3H_2O = \frac{\text{ml. } H_2SO_4 \times \text{N } H_2SO_4 \times \text{eq.wt. } PbAc_2.3H_2O \times 100}{1000 \times \text{ml. } PbAc_2.3H_2O}$$

Figure 4.-- Unit for the steam distillation of hop oil. (Note the inverted Y-tube leveling device between the oil trap and flask.)

and Connery [8/] using the assembly shown in figure 4. Added to the still are 700 ± 1 g. of green hops. Hot tap water is also added until the level is near the middle of the flask. The apparatus is connected, the oil trap

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8/ Wright, R. G. and Connery, F. E., Studies of Hop Quality. Amer. Soc. Brew. Chemists Proc. pp. 87-101 (1951)

filled with tap water, and the water in the graduated part of the trap adjusted to a safe level by means of the Y-tube leveling device. The distillation flask is covered with an asbestos blanket to prevent excess refluxing. The complete distillation requires 6 hours. After insuring that no oil droplets are adhering to the walls of the trap and that no water is in the oil layer[9/], the top meniscus of the oil layer is adjusted to 0 by means of the leveling device. The amount of oil collected is recorded and calculated as follows:

$$\text{ml. oil/100 g. hops (dry basis)} = \frac{\text{ml. oil collected}}{\text{sample wt. x pct. dry matter}} \times 100 \quad (6)$$

where "percent Dry Matter" is found from the separate moisture determination already described. An example of this determination is given in the Appendix. If the oil sample is to be saved for further testing, it should be dried over sodium sulfate, sealed in a glass ampoule, and stored under refrigeration.

THE ANALYSIS OF DRY HOPS

At harvest it is often desirable to detect changes in quality which result from processing or handling. Since drying is the first processing stage, it becomes necessary to analyze dry hops. The procedures described here for green hops are well adapted to the analysis of dry hops, and the modifications required are minor.

Quality changes occurring during drying are of most general interest. This requires sampling from the kiln floor before and after the drying interval of interest. It should be noted that hand-picked field samples should not be used as the "original" sample and compared with dry hops which have been machine-picked. When sampling from a kiln floor, representative samples should be composited from several spots over the whole bed.

Baled hops seem to be remarkably uniform, and the usual sampling procedures are adequate for most purposes. If a high degree of precision is required, samples from several bales can be composited.

Prior to the analysis for α-acid, about 50 g. of dry hops are ground in a hand-operated food chopper and mixed well--10 g. of this are extracted, filtered, and so forth according to the procedures described for green hops. The aliquot of extract taken for the titration can be adjusted for the richness of the sample. The equation for the calculation is:

$$\text{Percent } \alpha\text{-acid (dry-basis)} = \frac{\text{ml. lead acetate x pct. lead acetate}}{\text{pct. dry matter x aliquot}} \times 948,$$

or:

$$\text{Percent } \alpha\text{-acid (as-is)} = \frac{\text{ml. lead acetate x pct. lead acetate}}{\text{aliquot}} \times 9.48.$$

9/ A piece of wire with a loop on one end can be manipulated in the trap to free droplets from the walls.

The determination of the oil content of dry hops is the same as described for green hops except that only a 300 g. sample is used. The calculation employs the same equation unless the oil content is to be on an "as-is" basis:

$$\text{ml. oil per 100 g. (as-is)} = \frac{\text{ml. oil collected}}{\text{sample weight}}$$

A smaller distillation receiver is required for the determination of percent dry matter in dry hops[10/]. The sample weight taken for dry hops is 30 g. The distillation time, precautions, and calculations are the same as described for green hops.

INTERPRETATION OF RESULTS

The interpretation of data accumulated by periodic analysis of a crop during the growing season will usually depend upon the disposition which is to be made of the product. If a buyer is interested in richness of the hops in α-acid or oil, then predominant attention will be paid to the appropriate curve in order that the harvest can be made at the optimum time. If, on the other hand, a grower has buyers with varied interests, he might use the accumulation curves to decide which fields best match the requirements of his contracts.

Literature concerning maturity series is scarce and often inconsistent, but those who have reported on this subject agree on two things: (1) The importance of harvesting during peak quality conditions is unanimously stressed. (2) The nature of the accumulation of quality factors varies widely among varieties (table 1). Peaks which occur will undoubtedly be found on different dates in different years and will very likely reach different maximum values. The shape of the curve, however, can be expected to remain fairly constant for a variety.

Table 1. Amount of quality factors normally present in ripe hops

Variety	Pct. α-acid	Mls.oil/100 g. dry matter	
		Fresh hops	Dried hops
Late Cluster	5.0 - 7.0	0.5 - 1.0	0.2 - 0.5
Fuggle	4.0 - 6.0	2.0 - 2.5	.5 - 1.5
Bullion or Brewers Gold	8.0 -11.0	3.5 - 4.0	2.0 - 2.5

10/ Sterling-Bidwell distillation receiver, 5 ml., 0.1 ml. graduations, 24/40 S/T outer joint, 29/42 S/T inner joint.

Late Cluster is the predominant variety in the United States. It normally contains 5 to 7 percent α-acid and from 0.2 to 0.5 ml. oil per 100 g. in the bale. Green (fresh) hops, contain 5 to 7 percent α-acid and 0.5 to 1.0 ml. oil per 100 g. when ripe. In a 4-year study conducted in the Willamette Valley of Oregon, Rabak[11/] found that the α-acid content of this variety reaches a maximum value sometime during the first 2 weeks in September. His results coincide with a study now under way at this station (figure 5). Wright and Connery[12/] have shown that the oil content rises throughout the harvest period and in some cases for a week following the usual harvest period. A single year's data from the Corvallis Station indicate that accumulation of oil in Late Cluster may extend up to 2 weeks after the normal harvest period.

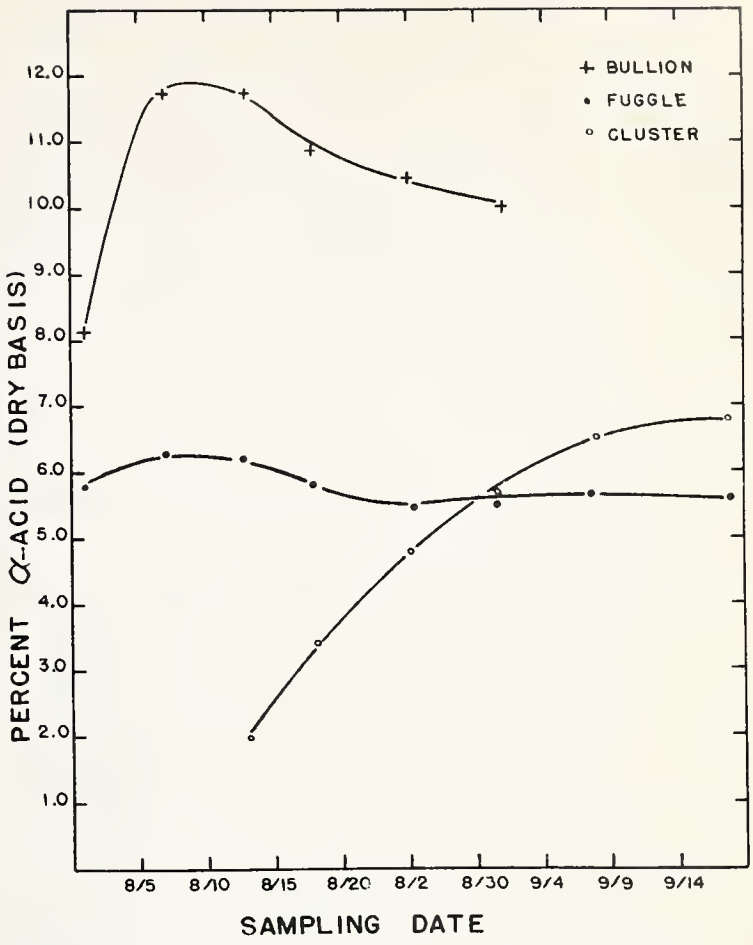

Figure 5.--Examples of the accumulation of α-acid in three varieties of hops.

The accumulation curves resulting from periodic sampling and analysis of Late Cluster are useful in two ways. Firstly, maturity can be determined by the shape of the curve -- when the quality factors (α-acid or oil) cease to increase, the crop is ready for harvest. To obtain maximum α-acid, for example, for the Late Cluster characterized in figure 5, the optimum harvest period would be from about September 9 to 19. Secondly, the quality potential of each field can be estimated, and its crop can be channeled so as to fill the appropriate contract.

Little information is available regarding the maturation characteristics of the variety Fuggle; however, data collected from two locations in the Willamette Valley during 1958 showed a relatively constant percentage of

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11/ Rabak, F., Relation of Time of Picking to the Quality of Hops. Paper presented at the 36th annual convention of the Master Brewers Association of America, held Oct. 15th to 19th, 1939.

12/ See footnote 8.

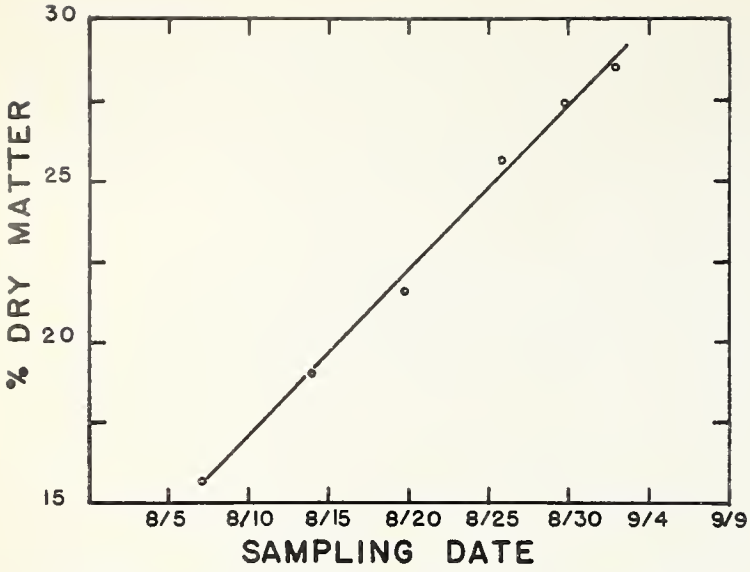

Figure 6.--The dry matter content of green hops as related to maturation. As the crop dries out it becomes more susceptible to shattering in the picking machine.

the richest field since no peak appears on the maturity curve to act as a guide to harvest date. Therefore, once a field has been selected for a particular contract, the initiation of harvest must be decided upon some basis other than α-acid analysis. Shattering is probably the next most important factor to be considered in producing high quality hops, assuming the field has been well managed and is free of insect and disease damage. The extent of drying out the crop has undergone during maturation is indicated by the percent-dry matter curve (figure 6). Generally, the percent-dry matter of Fuggle is about 25 percent at harvest, and values much higher might indicate excessive shattering could be expected[16/].

16/ The limiting value for percent-dry matter will vary slightly among localities and is best used as an aid to growers' judgment.

α-acid throughout the season. (figure 5). This indicates that α-acid and dry matter accumulated at approximately the same rate. Generally the α-acid content will lie between 4.5 and 6.0 percent. The oil content of Fuggle was found (again a single year's data) to reach a maximum value very near the usual harvest date and decline very little for about 3 weeks thereafter. Even though this information has not yet been confirmed, it provides a reasonable idea of what may be expected. When ripe, the oil content of the green cones will be from 2.0 to 2.5 ml. per 100 g. (dry-basis) while the dried cones range from 0.5 to 1.5 ml. per 100 g. (dry-basis), depending on initial values and processing losses.

If primary interest were in obtaining a Fuggle crop with a high α-acid content, periodic analysis would be useful only for selecting

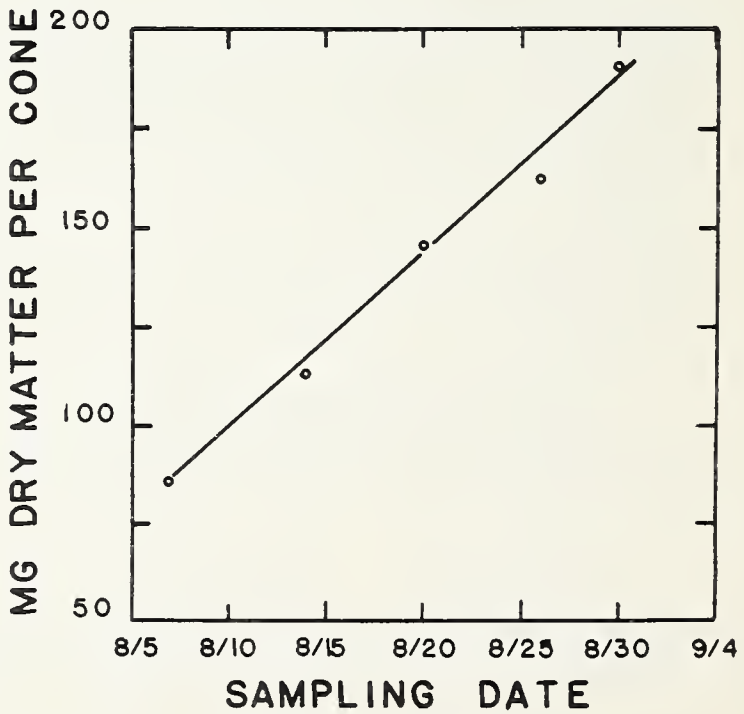

Figure 7.-- Accumulation of dry matter per cone. This indicates the actual growth of the crop. As long as the cone weight is increasing, final yield is increasing.

In the event that shattering is not considered a serious risk, the average cone weight (figure 7) will provide evidence concerning the growth of the crop. As long as the average cone weight is increasing, the yield potential of the crop is increasing.

If, on the other hand, the oil content of a Fuggle crop were of predominant interest, a maturity series would indicate a time of maximum oil content, and a decision regarding harvest date would be made on that basis. In such a case the other curves would only influence that decision in a secondary fashion; for example, if the percent dry matter indicated that the crop were unusually dry prior to maximum oil, a grower may wish to sacrifice some oil yield in order to avoid severe shattering.

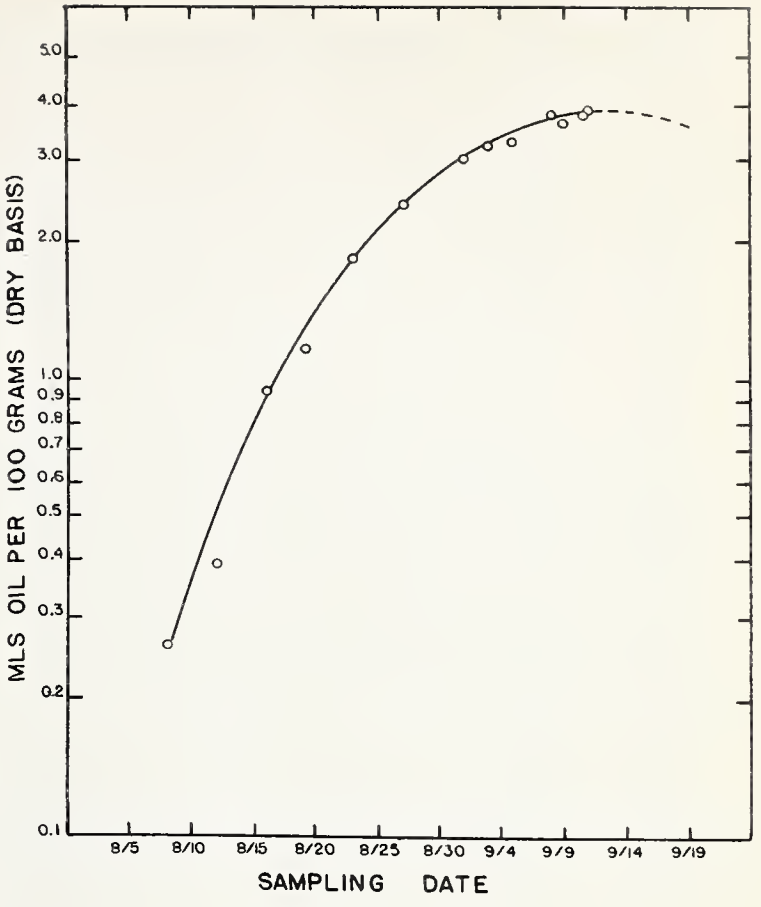

Figure 8.--Type of oil-yield curve which can be expected. This example is for the variety Bullion. Other varieties will have similar shaped curves but the amounts of oil present at maturity will vary widely.

The English varieties Bullion and Brewers Gold are not considered major varieties in the United States, but they are characterized by a third class of maturation curves, both from the standpoint of quantity of α-acid and oil, and the type of accumulation. When ripe, these varieties contain 8 to 11 percent α-acid. The oil content of the green cones ranges from 3 to 4 ml. per 100 g. (dry-basis), and freshly baled samples usually contain from 2 to 2.5 ml. per 100 g. (dry-basis). In contrast to both Late Cluster and Fuggle, α-acid appears to build up very fast as soon as the cones develop, then declines gently. In different years the α-acid peak varies somewhat from the example shown in figure 5, often appearing later in the season. Figure 8 illustrates an oil yield curve attributable to either of these varieties. Maximum α-acid can be estimated to within a few days and maximum oil can be estimated within 2 or 3 days. Like the other varieties discussed, the accumulation curves can also be used to compare fields for quality potential as an aid in determining the disposition of different lots of baled hops.

Further information on periodic sampling for the purpose of determining the proper harvest date can be found in a report by Hartong and Isebaert[17/].

17/ See footnote 4/.

The varieties with which they worked are not common to this country, but their data illustrate varietal differences very well.

APPENDIX

Complete Example of Collecting and Recording Data

The purpose of the following example is to illustrate the routine involved in analysis, the types of data sheets employed, and the methods of calculation. The types of graphs resulting from a series of such samples are shown in the text under INTERPRETATION OF RESULTS. (Figures 5, 6, 7, 8)

All weighings are made immediately to insure that the moisture content of all sub-samples is uniform at the time of weighing.

As soon as possible after a fresh sample arrives at the laboratory:

1. A serial number is assigned and the information necessary for identification is recorded on the "Work Sheet" (figure 9).

2. After thorough mixing, 700 g. are weighed, put into the flask for the oil determination and that weight recorded on the "Work Sheet".

3. 30 g. are weighed for α-acid determination and that weight recorded on the "Work Sheet".

4. 110.0 g. are weighed for the dry-matter determination and that weight recorded on the "Work Sheet". Without delay the cones are counted as they are put into the 1 liter flask, the number of cones is recorded, toluene is added to the flask, the distillation apparatus assembled, and the distillation begun. <u>This operation must be done quickly in order to minimize loss of moisture between weighing the sample and closing the apparatus. All calculations depend upon the correct value for the percent-dry matter</u>.

5. Water can now be added to the flask for the oil determination and the distillation can be started.

6. Chloroform can be added to the α-acid sample and that determination can be started. The amount of chloroform used for extraction and the aliquot taken for titration are recorded (along with the serial number of the sample) on the titration data sheet (figure 10).

MATURITY SERIES WORK SHEETS

Serial Number	Date	Location	Variety	Dry Matter				Cone Weight		Oil Yield			α-Acid						Remarks:
				wt. green	mls H_2O	grams D.M.	% D.M.	No. cones	mg per cone	wt. green	mls oil	mls per 100g	wt.	vol.	aliq.	% $PbAc_2$	mls	% α	
1	8/28/57	OSC BB311	Bull	110.0	82.7	27.3	24.8	182	149	700	3.95	2.28	30	100	15	4.26	2.99	10.8	Cldy; 65-70°F, no rain

Figure 9.--An example of a master work sheet which can be used to make all pertinent information about a sample, easily accessible, and at the same time serve as a data recording sheet.

CONDUCTOMETRIC DETERMINATION OF ALPHA-ACID ON GREEN HOPS

TITRATION DATA SHEET

Serial No Standard			Serial No 1			Serial No		
Weight —			Weight 30 g			Weight		
Volume —			Volume 100 mls			Volume		
Aliquot 4.0 mls 0.1N H_2SO_4			Aliquot 15 "			Aliquot		
% PbAc			% PbAc 4.26			% PbAc		
Date 8/28/59			Date 8/28/59			Date		
mls $PbAc_2$	$\Omega \times 10^{-5}$	$1/\Omega \times 10^5$	mls $PbAc_2$	$\Omega \times 10^{-5}$	$1/\Omega \times 10^5$	mls $PbAc_2$	$\Omega \times 10^{-5}$	$1/\Omega \times 10^5$
1.00	0.107	6.82	0	0.157	6.37			
1.25	0.153	4.77	0.50	0.152	6.58			
1.50	0.258	2.88	1.00	0.155	6.45			
1.75	0.913	0.80	1.50	0.157	6.37			
2.00	0.838	0.87	2.00	0.157	6.37			
2.25	0.459	1.59	2.50	0.158	6.33			
2.50	0.346	2.11	3.00	0.157	6.37			
2.75	0.269	2.71	3.50	0.143	6.99			
			4.00	0.132	7.56			
end point = 1.78 mls			4.50	0.121	8.26			
			5.00	0.113	8.70			
			end point = 2.99 mls					

Figure 10.--A mimeographed data sheet for titration data. Only the results of the determination need to be copied on the master work sheet.

The actual titration data and conversions to conductance are also recorded on this sheet. After the graph (figure 11) is constructed and the end point located, all pertinent information is transferred to the "Work Sheet". The calculation must wait for results from the "dry matter" determination.

7. After about 2 hours, the toluene distillation can be discontinued. After cooling to near room temperature, the ml. water can be read and recorded on the "Work Sheet". For sample No. 1 on the sample "Work Sheet" the calculation according to equations (1) and (2) is:

$$\frac{110.0 - 82.2}{110.0} = 24.8 \text{ percent dry matter.}$$

8. The α-acid calculation can now be made for the same example and according to equation (4) is as follows:

$$\frac{2.99 \times 4.26 \times 21.0}{24.8} = 10.8 \text{ percent } \alpha\text{-acid.}$$

9. After 6 hours of distillation the oil stills can be shut off and, after taking the precautions listed on pages 7-9, the ml. oil are recorded on the "Work Sheet." According to equation (6), the calculation for the sample problem is:

$$\frac{100 \times 3.95}{700 \times 24.8} = 2.28 \text{ ml. oil/100 g. dry hops.}$$

10. The cone weight calculation according to equation (3) is:

$$\frac{110.0 \times 24.8 \times 10}{182} = 149 \text{ mg. dry matter per cone.}$$

11. Data resulting from these determinations are plotted on the graphs which are maintained for the field from which the sample came (see figures 5, 6, 7, 8, under INTERPRETATION OF RESULTS).

12. An example of standardization of the lead acetate reagent is also given on the titration data sheet. In order to simplify the construction of the graph (figure 12), only the values beyond 1.00 ml. lead acetate are plotted. In this example the end point was found to be 1.78 ml. and according to equation (5) the strength of the reagent is:

$$\frac{7.58}{1.78} = 4.26 \text{ percent lead acetate}$$

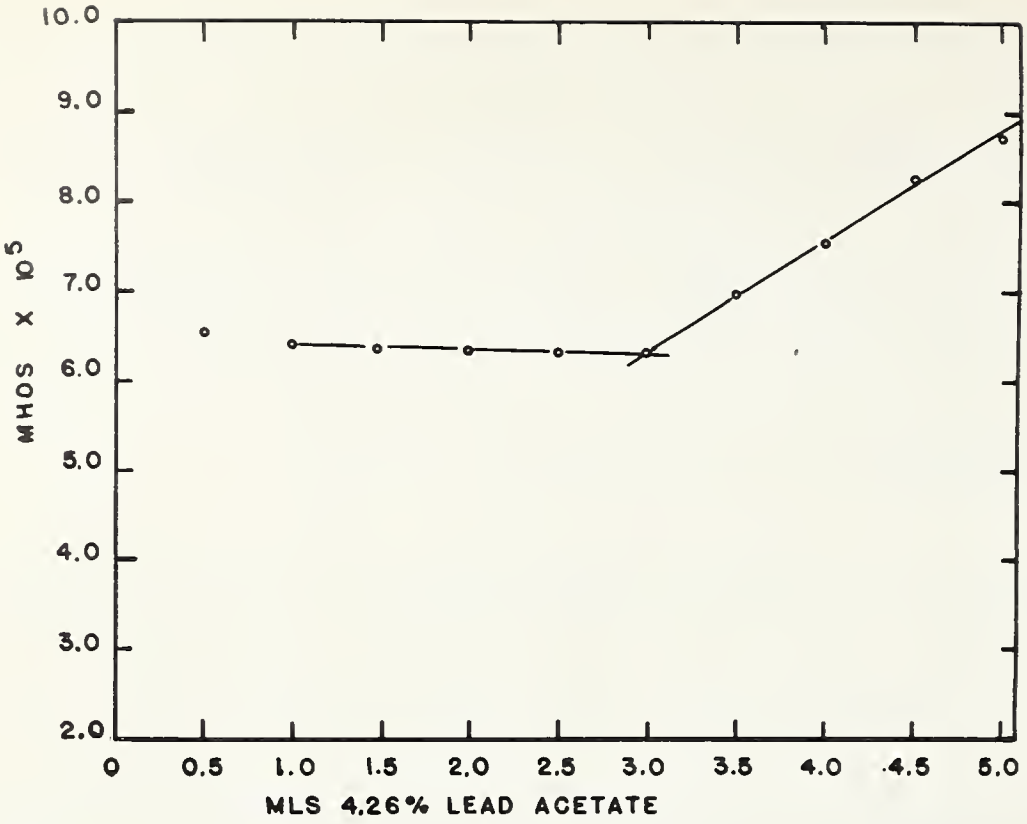

Figure 11.--Graph of the conductometric titration of α-acid for the example described in the text.

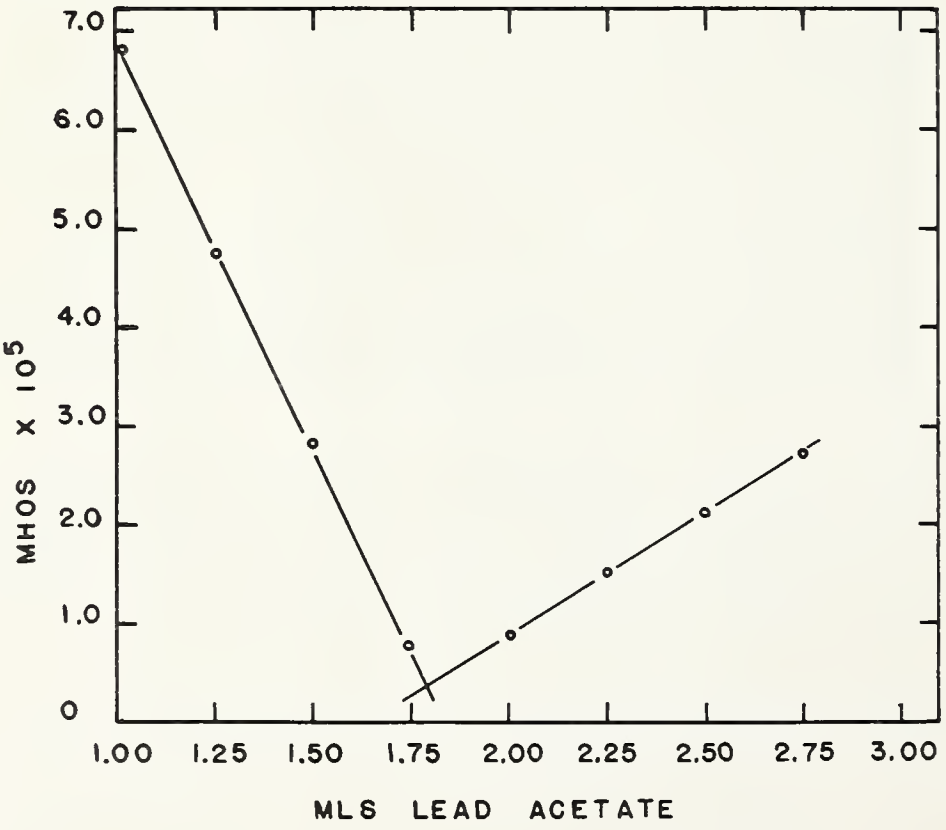

Figure 12.--Graph of conductivity (mhos) versus ml. lead acetate for the standardization of the titrant using 0.10 N H_2SO_4 as the standard (see text).

Cleaning of Equipment

The oil distillation flasks only need to be rinsed with tapwater. The traps can be rinsed with methanol or acetone followed by water. Occasionally they may require stronger cleaning with an agent such as dichromate-sulfuric acid solution.

Toluene distillation flasks and traps can be flushed with hot water, then rinsed with methanol or acetone. They must then either be allowed to dry or be rinsed with toluene to insure that no water is introduced into the next sample.

The homogenizer, funnels, and collection vessels used in the extraction of α-acid can be rinsed with methanol or acetone after flushing with hot water. Equipment used in the actual titration must first be rinsed with a 50:50 mixture of 28 percent acetic acid and toluene, which can, in turn, be removed with methanol. It is very important to rinse all residues of acetic acid if the ensuing titration is to be satisfactory.

Facilities, Equipment, and Reagents for the Analysis of Green Hops

Facilities:

1. 1 - 20 amp. circuit for each 2 oil stills.
2. 1 - 20 amp. circuit for each 4 moisture stills.
3. 1 - 20 amp. circuit for other uses.
4. Sink with hot and cold water.
5. Cold water tap for stills (preferably with a constant pressure control).
6. Cold water tap for an aspirator.
7. Facilities for safe disposal of waste solvents not miscible with water.
8. Good ventilation.

Item	Supplier ref. no.[a]	Approximate price (1960)[b] Dollar
General labware:		
1. Balance with 1,000 g. capacity and ± 0.1 g. sensitivity	1	21.00
2. Interval timer capable of operating a 20 amp. circuit in 6 hour intervals (1 each 2 oil stills and 1 for each 4 moisture stills)	2	10.00 ea.
3. Volumetric flasks:		
2-100 ml	1	4.00
1-250 "	1	2.00
1-500 "	1	3.00
2-1000 "	1	6.00

Item	Supplier ref. no.[a]	Approximate price (1960)[b] Dollar
4. Volumetric pipettes:		
1-1 ml.	1	1.00
1-2 "	1	1.00
1-3 "	1	1.00
1-4 "	1	1.00
1-5 "	1	1.00
1-10 "	1	1.00
1-15 "	1	1.00
1-20 "	1	1.00
1-25 "	1	1.00
1-50 "	1	2.00
1-100 ml.	1	2.00
5. Measuring pipettes:		
1-2 ml.	1	1.00
1-5 "	1	1.00
1-10 "	1	1.00
6. Stoppers - neoprene:		
1 lb. each #3, #4, #5, and #11	1	10.00
7. Wash bottles, polyethylene, 5 ml., 4 each	1	8.00
8. Clamps:		
6-Burette (spare supply, above needs of individual units	1	9.00
6-Universal with extension (spare supply, above needs of individual units)	1	12.00
9. Tubing:		
100 ft. Tygon, 3/16" I.D.	1	21.00
40 ft. glass, 10 mm. I.D.	1	2.00
10. Beakers:		
12-250 ml.	1	3.00
11. Erlenmyer flasks:		
12-125 ml.	1	4.00
12. 1-Spatula, 4"	1	1.00
13. 1-Burner, (Propane torch)	3	5.00
Sample collection:		
3-Water pail, 12 or 14 qt.	3	5.00
1-Ctn. (500 ea.) Polyethylene bags 12" x 8" x 30", 2 mil.	4	23.00
Labels, tags, etc.	3	5.00

a/See supplier reference last page of this report.

b/For total number of items unless otherwise specified.

Item	Supplier ref. no.[a]	Approximate price (1960)[b] Dollar
Moisture distillation (single set-up):		
1-Hot plate, 450 watts	1	14.00
1-Boiling flask, flat bottom, short neck, 29/42 S/T	1	3.00
1-Special Sterling-Bidwell distillation receiver with 75 ml. bulb, graduated from 75 to 100 ml. in 0.1 ml. increments. S/T joints: 24/40 outer, 29/42 inner	5	16.00
1-Liebig condenser, 300 mm., 24/40 S/T inner joint	1	7.00
1-Ring stand, (36" rod)	1	4.00
1-Universal clamp	1	2.00
1-Burette clamp	1	2.00
Tygon tubing		[c]
Alpha-acid:		
1-Homogenizer (Waring Blendor)	1	44.00
1-Homogenizer cup, aluminum, with screw-cap and sampling plug	1	30.00
1-Funnel (carbon-filter tube, 33 mm. I.D.)	6	1.00
Cotton		1.00
1-Conductivity bridge	1,7,8	225.00
1-Dip cell, glass, with cell constant of about 0.1 or 1.0	1,7,8	35.00
1-Stirrer (magnetic preferred)	1	35.00
1-Burette, 5 ml. with 0.02 ml. graduation	1	10.00
1-Ring stand, 36-inch rod	1	4.00
3-Burette clamps	1	2.00
1-Thermometer, -10°to 110°C.,	1	2.00
Oil distillation: (single set-up):		
1-Ring stand, 36 inch rod	1	4.00
1-Hot plate, 750 watts	1	25.00
1-Boiling flask, short neck, 12 liters	1	8.00
Tubing, glass, 10 mm., I.D.	1	[c]
Tubing, tygon, 3/6 mm., I.D.	1	[c]
Stoppers, neoprene, size 3 and 12	1	[c]
1-Condenser, 40 cm., Liebig	1	6.00
1-Connecting tube, glass, U-shaped, for tubing 3/16-inch diam.	1	1.00

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[c]/See general labware, item 9.

Item	Supplier ref. no.[a/]	Approximate price (1960)[b/] Dollar	
Oil distillation: (single set-up): (cont.)			
1-Oil trap, special design, see figure 4----------			
2-Universal clamps----------1		4.00	
1-Burette clamp----------1		2.00	
1-sq. yard asbestos cloth----------1		8.00	
Ampoules----------1		1.00	doz.
Reagents and solvents:			
Toluene------1 gal. per 16 moisture determinations----------1		3.86	per gal.
Methanol-----5 gal., tech. grade, for general washing and rinsing--------1		8.35	per 5 gal.
Methanol-----1 gal., reagent grade, per 50 α-acid determinations----------1		4.46	per gal.
Chloroform---1 lb., (300 ml.), reagent grade, per 3 α-acid determinations--------1		6.92	per 7.7 lbs. (5 pts.)
Lead acetate-1 lb., reagent grade----------1 [$Pb(C_2H_3O_2)_2.3H_2O$]		1.62	per lb.
Acetic acid--5 lb., reagent grade----------1		4.95	per 5 lb.

Following is a list of possible sources of supply for the various items listed in this appendix section.[d/] The supplier number given as follows corresponds to the reference number following the description of the item.

Supplier Ref.No.	Possible source of supply
1.	Most scientific supplies firms.
2.	Herbach and Rademan Inc., 1204 Arch St., Philadelphia 7, Pa.

d/ This listing does not imply endorsement by the USDA and may not be used in any advertisement. It is included only for the sake of convenience in equipping a new laboratory.

Supplier Ref.No.	Possible source of supply
3.	Obtainable locally.
4.	Kordite Corp., Macedon, N. Y.
5.	Scientific Glass Apparatus Co., 100 Lakewood Terrace, Bloomfield, N. J.
6.	Central Scientific Company, 1700 Irving Park Rd., Chicago 13, Ill.
7.	Radiometer, 72 Emdrupriej, Copenhagen NV, Denmark. (USA outlet: Welwyn International Inc., 3355 Edgecliff Terrace, Cleveland 11, Ohio.)
8.	Leeds and Northrup, 4907 Stenton Ave., Philadelphia 44, Pa.